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Preparation of Cyclic Carbonates from Alkadienols, CO_2, and Aryl or Vinylic Halides Catalyzed by a Palladium Complex

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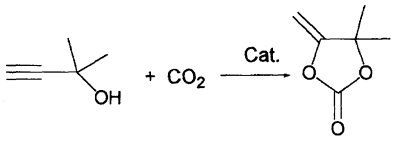
A novel three-component reaction of alkadienol, CO_2, and aryl or vinylic halide gives a vinyl group-substituted cyclic carbonate in one pot in the presence of a catalytic amount of a palladium complex. 2,3-Alkadienol affords five-membered ring carbonate in good yield, while 3,4-alkadienol effects the six-membered one successfully. 2,4-Alkadienol also takes part in this reaction to provide five-membered ring carbonate. A reaction pathway involving a π-allylic palladium species as an intermediate has been presumed.

The chemistry of CO_2 has received much attention from the viewpoint of carbon resources and environmental problems.[1] A large number of studies have been devoted to the fixation of CO_2 as carbonates and polycarbonates. Five-membered ring carbonates are obtained from the reaction of CO_2 with

i) oxiranes in the presence of various catalysts,[2] such as amines, halides, alkali salts, and phosphines;

ii) propargylic alcohols catalyzed by Cu,[3] Ru,[4] Pd,[5] Co[6] or P[7] compounds (Eq. 1), and



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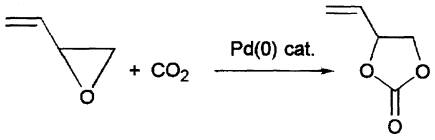
iii) vinyloxiranes in the presence of a Pd(0) complex[8] (Eq. 2).



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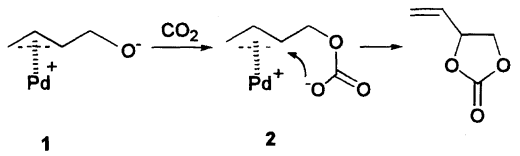
The products of iii) are regarded as being *cis* hydroxylation equivalents of vinyloxiranes, and can be used as synthetic intermediates.[8b] The preparation of six-membered ring carbonates from CO_2, on the other hand, is scarcely reported. For example, the synthesis of trimethylene carbonate, starting from CO_2 and oxetane in the presence of tetraphenylstibonium iodide, has been demonstrated.[9]

The intermediate of reaction iii) has been supposed to be the π-allylic palladium species **1**.[8] CO_2 reacts with the alkoxide in **1** to afford carbonate species **2**, which subsequently cyclizes to produce the five-membered ring carbonate (Eq. 3). Another route to generate the π-allylic palladium species **1** may involve the addition of 2,3- or 2,4-alkadienic compounds bearing hydroxy functionality as internal nucleophile, to palladium(II) species RPdX generated from RX and palladium(0) via oxidative addition,[10] where RX represents aryl or vinylic halide (Eq. 4). Generally, the protocol to utilize alkadienes, aryl or vinylic halides, and nucleophiles to afford products containing all three moieties has proved to be feasible.[11] Thus, several palladium-catalyzed cyclization reactions, including the formation of carbocyclic products starting from alkadienes bearing internal carbon nucleophiles and aryl or vinylic halides, have been realized according to this protocol.[12]



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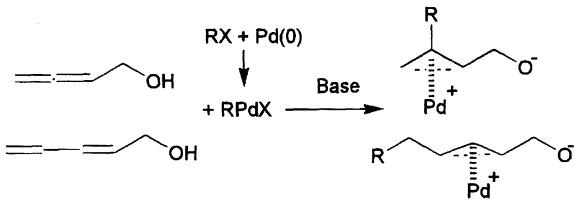

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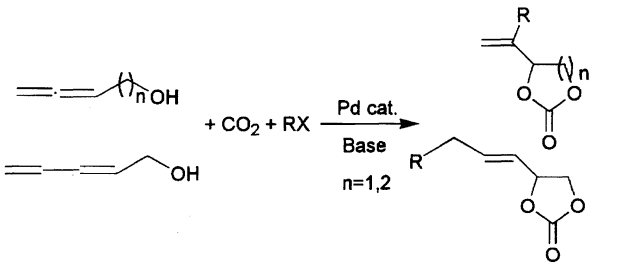
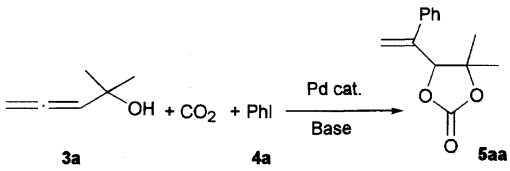
Here, we report on the palladium-catalyzed preparation of five- and six-membered ring carbonates starting from alkadienols, CO_2, and aryl or vinylic halides based on this approach (Eq. 5).



(5)

Results and Discussion

Preparation of Five-Membered Ring Carbonates from 2,3-Alkadienols, CO_2, and Aryl or Vinylic Halides. At first, the reaction of 2-methyl-3,4-pentadien-2-ol (**3a**), CO_2, and phenyl halide **4** was selected as a probe to examine the feasibility. Using 5 mol% of $[Pd(PPh_3)_4]$ as a catalyst, a mixture of **3a** and phenyl iodide (**4a**) was heated at 100 °C for 8 h in the presence of a base under CO_2 pressure. The procedure afforded the anticipated five-membered ring carbonate **5aa** (Eq. 6). The results are given in Table 1. The use of NaH as a base and THF as a solvent led to a miserable result (Entry 1). The utilization of K_2CO_3 as a base and *N*, *N*-dimethylacetamide (DMAc) as a solvent resulted in a great improvement in the yield (Entry 2). Phenyl bromide (**4b**) could be employed instead of phenyl iodide along with a slight decline in the yield, but phenyl chloride (**4c**) did not afford **5aa** (Entries 3 and 4). Equally good results were achieved with the palladium(II) complex, $[PdCl_2(PPh_3)_2]$ (Entry 5). The reaction was quite sluggish at a lower reaction temperature of 50 °C or below (Entries 6 and 7). Thus, the following conditions were selected as the standard: 1 equiv of dienol, 1 equiv of aryl or vinylic halide, 1.5 equiv of K_2CO_3, 5 mol% of $[PdCl_2(PPh_3)_2]$, 1 cm^3 solvent (DMAc) per 0.25 mmol of dienol, 40 atm, 100 °C, 8 h. Since K_2CO_3 dissolves in DMAc only sparingly, the reaction is heterogeneous.



(6)

Using the above conditions, we explored the generality of the reaction by varying aryl or vinylic halides and alkadienols **3**. In Table 2, the results of the reaction of **3a** with CO_2 and various aryl or vinylic halides are summarized. 1-Naphthyl (**4d**), 2-naphthyl (**4e**), 4-nitrophenyl (**4f**), and α-styryl (**4j**) bromides took part in this reaction satisfactorily (Entries 1, 2, 3, and 7). The substituted phenyl bromide bearing an electron-donating substituent of methyl (**4g**) or methoxyl (**4h**) group afforded the carbonate (**5ag** or **5ah**) in moderate yield. This result may be ascribed to the reduced reaction rate at the oxidative addition step where ArPdBr is generated (Eq. 4).[13] Interestingly, the OH group is compatible, albeit the yield is unsatisfactory (Entry 6). Only the *trans* isomer of **5ak** was obtained selectively in a moderate yield of 55%

Table 1. Preparation of **5aa** from **3a**, CO_2, and Phenyl Halide **4**[a]

Entry		4	Base	Solvent	Pd complex	CO_2 (atm)	Temp (°C)	Yield (%)[b]
1	**4a**	PhI	NaH[c]	THF	$[Pd(PPh_3)_4]$	10	100	[d]
2	**4a**	PhI	K_2CO_3	DMAc	$[Pd(PPh_3)_4]$	40	100	99(88)
3	**4b**	PhBr	K_2CO_3	DMAc	$[Pd(PPh_3)_4]$	40	100	90
4	**4c**	PhCl	K_2CO_3	DMAc	$[Pd(PPh_3)_4]$	40	100	0
5	**4a**	PhI	K_2CO_3	DMAc	$[PdCl_2(PPh_3)_2]$	40	100	99
6	**4a**	PhI	K_2CO_3	DMAc	$[PdCl_2(PPh_3)_2]$	40	50	12
7	**4a**	PhI	K_2CO_3	DMAc	$[Pd(PPh_3)_4]$	40	R.T.	0

a) **3a** 1.0 mmol, **4** 1.0 mmol, K_2CO_3 1.5 mmol, solvent 2 cm^3, Pd complex 0.02 mmol; 8 h. b) GLC Yield. Yield in parentheses is for isolated compound. c) Sodium alkoxide prepared from **3a** and NaH (1.0 equiv) was used. d) Small amount of several products including **5aa** and 1,1-dimethyl-2-(1-phenylethenyl)oxirane.

Table 2. Preparation of **5** from **3a**, CO_2, and Organic Halide **4**[a]

Entry		4	5	Yield (%)
1	**4d**	1-Naphthyl Bromide	**5ad**	82
2	**4e**	2-Naphthyl Bromide	**5ae**	94
3	**4f**	4-Nitrophenyl Bromide	**5af**	92
4	**4g**	4-Methylphenyl Bromide	**5ag**	54
5	**4h**	4-Methoxyphenyl Bromide	**5ah**	49
6	**4I**	4-Hydroxyphenyl Bromide	**5ai**	19
7	**4j**	α-Styryl Bromide	**5aj**	80
8	**4k**	β-Styryl Bromide (*trans* : *cis* = 88 : 12)	**5ak**	55 (*trans* isomer only)

a) A mixture of **3a** (2 mmol), **4** (2 mmol), K_2CO_3 (3 mmol), and $[PdCl_2(PPh_3)_2]$ (0.04 mmol) was stirred in DMAc (4 cm^3) under pressured CO_2 (40 atm) at 100°C for 8 h.

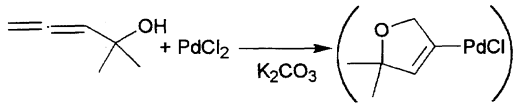
from β-styryl bromide (**4k**) of a *trans*, *cis* mixture (Entry 8).

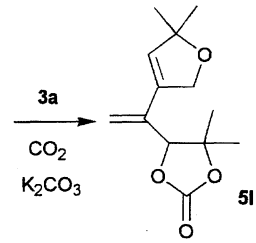
On the other hand, the results with alkyl halides were inconsistent. Benzyl bromide produced the corresponding carbonate in 41% yield. Methyl iodide afforded the expected carbonate in less than 7% yield together with the other several products. The anticipated carbonate was not obtained with butyl bromide.

The results obtained with various 2,3-alkadienols **3** and phenyl iodide (**4a**) are given in Table 3. The tertiary and secondary 2,3-alkadienols, **3a** and **3b**, reacted smoothly with CO_2 and phenyl iodide at 100 °C to afford the corresponding five-membered ring carbonates, **5aa** and **5ba**, in good yields (Entries 1 and 2). The primary alcohol **3c** did not afford the expected carbonate **5ca** at the reaction temperature of 100 °C, but produced an aldehyde, 3-phenyl-2-butenal in 23% yield.[8a] Since **5ca** could be obtained in 52% yield at a reaction temperature of 50 °C (Entry 3), **5ca** was supposed to suffer decarboxylation at a higher temperature. The alkadienols **3** bearing the Me or Ph substituent on the diene part reacted similarly well, affording the corresponding carbonates **5** in good yields (Entries 4, 5, 6, and 7).

We then studied the reaction from a different aspect. Product **5aa** is chiral. In order to realize asymmetric induction, a chiral ligand-coordinated complex [$PdCl_2$((S)-BINAP)] was employed as a catalyst (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl). This complex effected product **5aa** in 21% yield after 8 h at 50 °C starting from **3a**, CO_2, and **4a**. Unfortunately, the asymmetric induction was disappointingly low of 1%.

Besides the above catalytic examples, we also observed a similar type of cyclization of **3a** with CO_2, employing a stoichiometric amount of palladium(II) complex without utilizing aryl halide. When a mixture of an equimolar amount of **3a** and $PdCl_2$ was heated at 80 °C in DMAc in the presence of K_2CO_3 under the pressure of CO_2, a five-membered ring carbonate **5l** was formed in 62% yield (based on **3a**), which comprised 2 moles of **3a** and 1 mole of CO_2 (Eq. 7). We tentatively propose the intermediary formation of dihydrofurylpalladium species **4l** via a palladium mediated nucleophilic cyclization of **3a**, which would react in turn with the second molecule of **3a** and CO_2 to produce **5l**. In this connection, similar reactions of allene with nucleophiles such as amine,[14] acetic acid,[15] water,[16] and alcohol[16] to afford 2,3-dialkylbutadiene derivatives have been reported.

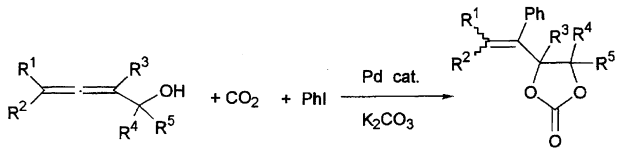




(7)

Preparation of Six-Membered Ring Carbonate from 3, 4-Alkadienols, CO_2, and Phenyl Iodide. To extend the scope, the reaction of one carbon-longer substrate, 3,4-alkadienols **6**, with CO_2 and phenyl iodide was then investigated (Eq. 8). The parent substrate, 3,4-pentadien-1-ol (**6a**), did not afford the expected six-membered ring, carbonate **7a**, at a reaction temperature of 100 °C. Product **7a** was barely obtained in 27% yield after 40 h by lowering the reaction temperature to 50 °C. Methyl-substituted substrates, **6b** and **6c**, reacted smoothly to give **7b** and **7c** in 62 (*trans* : *cis* = 80 : 20) and 70% yield, respectively, under the standard conditions. This is the first example concerning the preparation of vinyl group-substituted six-membered ring carbonates from CO_2, since they are usually prepared by a treatment of 4-penten-1,

Table 3. Preparation of **5** from 2,3-Alkadienols **3**, CO_2 and PhI (**4a**)[a]

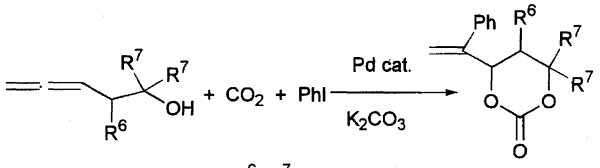


3 **4a** **5**

Entry		3 R¹	R²	R³	R⁴	R⁵		Yield of 5 (%)
1	**3a**	H	H	H	Me	Me	**5aa**	99
2	**3b**	H	H	H	H	Me	**5ba**	88 (*trans* : *cis* = 82 : 18)[c]
3[b]	**3c**	H	H	H	H	H	**5ca**	52
4	**3d**	Me	H	H	Me	Me	**5da**	82 (*E* : *Z* = 84 : 16)[c]
5	**3e**	Ph	H	H	Me	Me	**5ea**	72 (*E* : *Z* = 79 : 21)[c]
6	**3f**	Me	Me	H	Me	Me	**5fa**	72
7	**3g**	H	H	Me	Me	Me	**5ga**	93

a) A mixture of **3** (2 mmol), **4a** (2 mmol), K_2CO_3 (3 mmol), and [$PdCl_2(PPh_3)_2$] (0.04 mmol) was stirred in DMAc (4 cm^3) under pressured CO_2 (40 atm) at 100 °C for 8 h. b) 50 °C, 39 h. c) Stereochemistry was determined by NOE experiment.

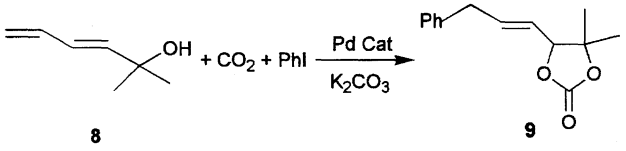
3-diols with alkyl chloroformate in the presence of a base.[17] It is noted that this type of carbonate is an excellent substrate for palladium-catalyzed carbonylation and polymerization reactions.[17]



6 a R^6=R^7=H b R^6=Me, R^7=H c R^6=H, R^7=Me 7

(8)

Preparation of Five-Membered Ring Carbonate from 2,4-Alkadienol, CO_2, and Phenyl Iodide. Finally, we investigated the feasibility of the reaction with 2,4-alkadienol instead of 2,3- or 3,4-alkadienol as substrate according to the protocol. The reaction of (*E*)-2-methyl-3,5-haxadien-2-ol (**8**) with CO_2 and phenyl iodide was sluggish at 100 °C. The reaction at 120 °C afforded five-membered ring carbonate (*E*)-**9** stereoselectively in a moderate yield of 48% after 20 h (Eq. 9).



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(9)

The approach mentioned above enabled the facile fixation of CO_2 producing vinyl group-substituted five- and six-membered ring carbonates using alkadienols and aryl or vinylic halides.

Experimental

General. IR spectra were recorded on a JASCO FT/IR 350 spectrometer. ^{1}H and ^{13}C NMR spectra were measured either on a Bruker DRX 500 or a DPX 400 spectrometer (500 and 125, 400 and 100 MHz, respectively) with $CDCl_3$ as a solvent with HMQC and (in certain cases) NOE experiments. GC-MS spectra were obtained on a Shimadzu GCMS-QP2000A apparatus. GLC analyses were performed with a Hitachi 263-30 Gas Chromatograph with a flame-ionization detector using Unisole 30T 2% on Uniport Hp. The melting points were uncorrected. The alkadienols **3**, **6**, and **8** were synthesized according to the reported methods.[18] Organic halides were commercially obtained. The palladium complexes were prepared in our laboratory. The ratio of stereoisomer was determined either by GLC or ^{1}H NMR.

General Procedure for the Preparation of Five-Membered Ring Carbonate 5 from Alkadienol 3. A mixture of **3** (2 mmol), aryl halide (2 mmol), [$PdCl_2(PPh_3)_2$] (0.04 mmol), K_2CO_3 (3 mmol), and DMAc (4 ml) was placed in an autoclave and heated at 100 °C under pressured CO_2 (40 atm). After 8 h, the mixture was taken up in diethyl ether and filtered. The organic layer was washed with 5 ml each of 1.0 M HCl for 5 times and 10 ml each of 2.0 M sodium sulfate for 3 times (1 M = 1 mol dm^{-3}). The organic layer was concentrated in vacuo and the residue was submitted to column chromatography on silica gel eluting with hexane/ethyl acetate to give **5**.

4,4-Dimethyl-5-(1-phenylethenyl)-1,3-dioxolan-2-one (5aa). Mp 59—61 °C. IR (KBr) 1799 (C=O), 1268, 1234, 1117, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.18 (s, 3H, one of Me_2), 1.34 (s, 3H, one of Me_2), 5.41 (d, J = 1.1 Hz, 1H, HC–O), 5.50 (s, 1H, one H of H_2C=), 5.57 (d, J = 1.1 Hz, 1H, the other H of H_2C=), 7.32—7.41 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 22.38, 26.98, 84.70, 84.82, 115.74, 126.79, 128.73, 128.95, 137.90, 141.07, 153.81; GC-MS (70 eV) *m/z* 43 (18), 77 (16), 103 (16), 115 (100), 116 (65), 218 (M^+; 27). Found: C, 71.66; H, 6.53%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%.

4,4-Dimethyl-5-[1-(1-naphthyl)ethenyl]-1,3-dioxolan-2-one (5ad). Mp 84—86 °C. IR (KBr) 1807 (C=O), 1640, 1268, 1051 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.08 (s, 3H, one of Me_2), 1.37 (s, 3H, one of Me_2), 5.36 (s, 1H, HC–O), 5.59 (s, 1H, one H of H_2C=), 5.98 (s, 1H, the other H of H_2C=), 7.34—8.05 (m, 7H, naphthyl); ^{13}C NMR ($CDCl_3$) δ = 22.27, 26.21, 85.03, 86.10, 119.3, 124.8—135.5, 139.3, 153.7; GC-MS (70 eV) *m/z* 43 (20), 153 (100), 165 (62), 268 (M^+; 7). Found: C, 75.80; H, 6.06%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.

4,4-Dimethyl-5-[1-(2-naphthyl)ethenyl]-1,3-dioxolan-2-one (5ae). Mp 99—101 °C. IR (KBr) 1800 (C=O), 1637, 1273, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.21 (s, 3H, one of Me_2), 1.36 (s, 3H, one of Me_2), 5.55 (s, 1H, HC–O), 5.64 (s, 1H, one H of H_2C=), 5.67 (s, 1H, the other H of H_2C=), 7.45—7.87 (m, 7H, Naphtyl); ^{13}C NMR ($CDCl_3$) δ = 22.53, 27.14, 84.77, 84.82, 116.26, 119.64, 124.64, 125.78, 126.79, 126.87, 127.76, 128.16, 128.89, 133.20, 135.28, 141.12, 153.69; GC-MS (70 eV) *m/z* 43 (29), 153 (37), 165 (100), 268 (M^+; 72). Found: C, 75.33; H, 6.08%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.

4,4-Dimethyl-5-[1-(4-nitrophenyl)ethenyl]-1,3-dioxolan-2-one (5af). Mp 101—103 °C. IR (KBr) 1794 (C=O), 1517, 1346, 1262, 859 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.20 (s, 3H, one of Me_2), 1.42 (s, 3H, one of Me_2), 5.46 (s, 1H, HC–O), 5.70 (d, J = 0.6 Hz, 1H, one H of H_2C=), 5.77 (d, J = 0.6 Hz, 1H, the other H of H_2C=), 7.58 (d, J = 8.8 Hz, 2H, meta H to NO_2 group), 8.27 (d, J = 8.8 Hz, 2H, ortho H to NO_2 group); ^{13}C NMR ($CDCl_3$) δ = 22.45, 26.89, 84.22, 84.56, 119.15, 124.13, 127.66, 139.72, 144.17, 147.72, 153.10; GC-MS (70 eV) *m/z* 43 (42), 115 (64), 161 (100), 263 (M^+; 12). Found: C, 59.23; H, 5.00; N, 5.26%. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32%.

4,4-Dimethyl-5-[1-(4-methylphenyl)ethenyl]-1,3-dioxolan-2-one (5ag). Mp 67—69 °C. IR (KBr) 1798 (C=O), 1634, 1268, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.16 (s, 3H, one of Me_2), 1.34 (s, 3H, one of Me_2), 2.35 (s, 3H, *Me*-C_6H_4), 5.42 (s, 1H, HC–O), 5.45 (s, 1H, one H of H_2C=), 5.50 (s, 1H, the other H of H_2C=), 7.16—7.25 (m, 4H, aromatic); ^{13}C NMR ($CDCl_3$) δ = 20.86, 22.06, 26.66, 84.46, 114.41, 126.39, 129.36, 134.67, 138.42, 140.81, 153.90; GC-MS (70 eV) *m/z* 43 (34), 115 (100), 129 (71), 232 (M^+; 38). Found: C, 72.23; H, 7.08%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

5-[1-(4-Methoxylphenyl)ethenyl]-4,4-dimethyl-1,3-dioxolan-2-one (5ah). Mp 67—69 °C. IR (KBr) 1800 (C=O), 1634, 1267, 1248, 1113, 1051 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.17 (s, 3H, one of Me_2), 1.35 (s, 3H, one of Me_2), 3.82 (s, 3H, MeO), 5.40 (s, 1H, HC–O), 5.46 (s, 1H, one H of H_2C=), 5.47 (s, 1H, the other H of H_2C=), 6.91 (d, J = 6.8 Hz, 2H, ortho H to OMe group), 7.27 (d, J = 6.8 Hz, 2H, meta H to OMe group); ^{13}C NMR ($CDCl_3$) δ = 22.01, 26.72, 55.01, 84.53, 113.85, 114.08, 127.76, 129.91, 140.37, 153.52, 159.73; GC-MS (70 eV) *m/z* 43 (53), 103 (74), 133 (100), 148 (70), 248 (M^+; 65). Found: C, 67.54; H, 6.56%. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50%.

5-[1-(4-Hydoxylphenyl)ethenyl]-4,4-dimethyl-1,3-dioxolan-2-one (5ai). IR (neat) 3390, 1792 (C=O), 1270, 1051 cm^{-1}; ^{1}H NMR

($CDCl_3$) δ = 1.18 (s, 3H, one of Me_2), 1.36 (s, one of Me_2), 5.36 (s, 1H, HC–O), 5.41 (s, 1H, one H of H_2C=), 5.46 (s, 1H, the other H of H_2C=), 5.70 (s, 1H, OH), 6.85 (d, J = 8.6 Hz, ortho H to OH group), 7.02 (d, J = 8.6 Hz, meta H to OH group); ^{13}C NMR ($CDCl_3$) δ = 22.27, 26.99, 84.95, 114.29, 115.81, 129.11, 130.10, 140.37, 156.31; GC-MS (70 eV) *m/z* 43 (59), 119 (63), 131 (100), 234 (M^+; 53). Found: C, 65.14; H, 5.73%. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02%.

4,4-Dimethyl-5-(1-methylene-2-phenyl-2-propenyl)-1,3-dioxolan-2-one (5aj). IR (neat) 1806 (C=O), 1267, 1113, 1054 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.36 (s, 3H, one of Me_2), 1.38 (s, one of Me_2), 4.95 (s, 1H, HC–O), 5.32 (s, 1H, one H of either H_2C=), 5.37 (s, 1H, the other H of the H_2C=), 5.51 (s, 1H, one H of the other H_2C=), 5.65 (s, 1H, the other H of the other H_2C=), 7.29—7.50 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 21.83, 26.43, 83.45, 84.62, 116.13, 117.97, 127.47, 128.47, 128.76, 138.66, 141.27, 148.01, 153.67; GC-MS (70 eV) *m/z* 43 (73), 129 (100), 185 (53), 244 (M^+; 1). Found: C, 73.15; H, 6.58%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

(*E*)-4,4-Dimethyl-5-(1-methylene-3-phenyl-2-propenyl)-1,3-dioxolan-2-one (5ak). IR (neat) 1804 (C=O), 1603, 1266, 1061 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.31 (s, 3H, one of Me_2), 1.67 (s, one of Me_2), 5.22 (s, 1H, HC–O), 5.44 (s, 1H, one H of H_2C=), 5.54 (s, 1H, the other H of H_2C=), 6.56 (d, J = 16.6 Hz, 1H, PhC*H*=), 6.76 (d, J = 16.6 Hz, 1H, *H*C=CPh), 7.25—7.43 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 22.47, 27.35, 83.52, 84.42, 116.7, 124.58, 128.10, 128.39, 130.15, 135.94, 138.70, 153.74; GC-MS (70 eV) *m/z* 43 (37), 129 (100), 244(M^+; 8). Found: C, 72.81; H, 6.89%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

4-Methyl-5-(1-phenylethenyl)-1,3-dioxolan-2-one (5ba). A mixture of *cis* and *trans* isomers. IR (neat) 1806 (C=O), 1642, 1187, 1072 cm^{-1}; GC-MS (70 eV) *m/z* 43 (32), 44 (31), 77 (44), 103 (100), 104 (40), 115 (97), 145 (40), 159 (41), 204 (M^+; 67). Found: C, 71.10; H, 6.18%. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92%.

***cis*-Isomer.** ^{1}H NMR ($CDCl_3$) δ = 1.12 (d, J = 7.1 Hz, Me), 4.94 (1H, quint, J = 7.1 Hz, Me*H*C–O), 5.57 (s, 1H, one H of H_2C=), 5.67 (s, 1H, the other H of H_2C=), 5.76 (d, J = 7.1 Hz, 1H, C=C–CH–O), 7.26—7.41 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ = 15.57, 76.16, 79.18, 115.18, 125.85, 128.77, 129.10, 136.81, 143.31, 154.20.

***trans*-Isomer.** ^{1}H NMR ($CDCl_3$) δ = 1.39 (d, J = 6.6 Hz, 3 H, Me), 4.41 (quint, J = 6.6 Hz, 1 H, Me*H*C–O), 5.10 (d, J = 6.6 Hz, 1H, C=C–CH–O), 5.49 (s, 1H, one H of H_2C=), 5.52 (s, 1 H, the other H of H_2C=), 7.26—7.41 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ = 19.51, 78.23, 83.75, 116.40, 127.10, 128.77, 128.92, 136.81, 143.31, 154.20.

4-(1-Phenylethenyl)-1,3-dioxolan-2-one (5ca). IR (neat) 1816 (C=O), 1170, 1073 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 4.08 (dd, J = 7.2 and 8.4 Hz, 1H, one of H_2C–O), 4.59 (t, J = 8.4 Hz, 1H, one of H_2C–O), 5.52 (d, J = 1.3 Hz, 1H, one H of H_2C=), 5.54 (s, 1H, the other H of H_2C=), 5.61 (ddd, J = 1.3, 8.4, and 7.2 Hz, C=C–CH–O), 7.29—7.31 (m, 2 H, ortho H of Ph), 7.36—7.38 (m, 3 H, meta and para H of Ph); ^{13}C NMR ($CDCl_3$) 69.21, 76.89, 115.26, 126.57, 128.79, 128.97, 136.32, 143.33, 154.78; GC–MS (70 eV) *m/z* 44 (26), 51 (27), 77 (34), 103 (100), 104 (56), 115 (27), 190 (M^+; 52). Found: C, 69.33; H, 5.36%. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30%.

4,4-Dimethyl-5-(1-phenyl-1-propenyl)-1,3-dioxolan-2-one (5da). A mixture of *E* and *Z* isomers. IR (neat) 1802 (C=O), 1644, 1269, 1237, 1120, 1095 cm^{-1}; GC-MS (70 eV) *m/z* 43 (22), 91 (15), 115 (100), 117 (19), 128 (20), 129 (92), 130 (34), 232 (M^+; 21). Found: C, 72.20; H, 7.28%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

(*Z*)-Isomer. ^{1}H NMR ($CDCl_3$) δ = 1.27 (s, 3 H, one of Me_2), 1.46 (s, 3 H, one of Me_2), 1.90 (d, J = 7.3 Hz, MeC=), 5.47 (s, 1 H, HC–O), 5.91 (q, J = 7.3 Hz, 1 H, HC=), 7.26—7.31 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ = 14.26, 22.65, 27.53, 83.75, 85.13, 127.51, 128.30, 128.38, 131.72, 134.59, 139.85, 153.80.

(*E*)-Isomer. ^{1}H NMR ($CDCl_3$) δ = 1.16 (s, 3 H, one of Me_2), 1.25 (s, 3 H, one of Me_2), 1.69 (dd, J = 7.0 and 1.5 Hz, 3 H, MeC=), 5.15 (quint, J = 1.5 Hz, 1 H, HC–O), 6.06 (dq, J = 7.0 and 1.5 Hz, 1 H, HC=), 7.19—7.41 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ = 13.99, 22.13, 26.28, 84.92, 86.94, 125.17, 127.79, 128.55, 129.04, 132.61, 135.73, 153.62.

5-(1,2-Diphenylethenyl)-4,4-dimethyl-1,3-dioxolan-2-one (5ea). **(*E*)-Isomer.** Mp 124—126 °C. IR (KBr) 1807 (C=O), 1651, 1266, 1116, 1070, 1020 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 1.09 (s, 3 H, one of Me_2), 1.32 (s, 3 H, one of Me_2), 5.67 (s, 1 H, HC–O), 6.83 (s, 1 H, HC=), 6.99—7.38 (m, 10 H, Ph); ^{13}C NMR (DMSO-d_6) δ = 22.40, 26.03, 85.47, 86.50, 127.88, 128.03, 128.61, 128.93, 129.50, 129.57, 129.80, 133.95, 135.78, 136.44, 153.42; GC-MS (70 eV), *m/z* 43 (40), 44 (42), 180 (23), 191 (100), 192 (82), 219 (21), 294 (M^+; 53). Found: C, 77.61; H, 6.24%. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16%.

(*Z*)-Isomer. The ^{1}H NMR spectrum was taken as an (*E*+*Z*) mixture. ^{1}H NMR ($CDCl_3$) δ = 1.36 (s, 3 H, one of Me_2), 1.40 (s, 3 H, one of Me_2), 5.55 (s, 1 H, HC–O). The olefinic and aromatic protons occur in the region of 7.21—7.52 ppm.

4,4-Dimethyl-5-(2-methyl-1-phenyl-1-propenyl)-1,3-dioxolan-2-one (5fa). IR (neat) 1799 (C=O), 1644, 1268, 1227, 1117, 1038 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.37 (s, 3 H, one of Me_2C–), 1.49 (s, 3 H, one of Me_2C–), 1.59 (s, 3 H, one Me of Me_2C=), 1.86 (S, 3 H, the other Me of Me_2C=), 5.42 (s, 1 H, HC–O), 7.17—7.33 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ = 20.39, 22.29, 22.92, 27.64, 84.03, 84.92, 126.97, 127.77, 128.76, 130.57, 136.83, 137.04, 153.64; GC-MS (70 eV) *m/z* 44 (29), 91 (17), 128 (30), 129 (100), 143 (22), 246 (M^+; 23). Found: C, 72.93; H, 7.36%. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37%.

4,4,5-Trimethyl-5-(1-phenylethenyl)-1,3-dioxolan-2-one (5ga). Mp 60—62 °C. IR (KBr) 1796 (C=O), 1645, 1271, 1180, 1056, 1016 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.37 (s, 3H, one of Me_2), 1.43 (s, 3H, one of Me_2), 1.68 (s, 3H, =C–CMe), 5.27 (s, 1H, one H of H_2C=), 5.61 (s, 1H, the other H of H_2C=), 7.28—7.34 (m, 5H, Ph); GC-MS (70 eV) *m/z* 41 (23), 43 (55), 44 (35), 51 (22), 77 (33), 103 (41), 115 (98), 129 (100), 130 (99), 146 (21), 232 (M^+;11). Found: C, 72.38; H, 7.41%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

Reaction of 3a with CO_2 and Benzyl Bromide. The reaction was performed according to the general procedure.

4,4-Dimethyl-5-(1-benzylethenyl)-1,3-dioxolan-2-one. IR (neat) 1799 (C=O), 1268, 1058 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.44 (s, 3H, one of Me_2), 1.63 (s, 3H, one of Me_2), 3.27 (d, J = 14.3 Hz, one H of CH_2), 3.53 (d, J = 14.3 Hz, the other H of CH_2), 4.75 (s, 1H, HC–O), 5.23 (s, 1H, one H of H_2C=), 5.42 (s, 1H, the other H of H_2C=), 7.20—7.41 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 21.46, 26.38, 38.83, 83.47, 84.80, 115.04, 126.15, 127.96, 128.25, 136.18, 139.88, 153.70; GC-MS (70 eV) *m/z* 43 (45), 91 (79), 115 (74), 129 (100), 232 (M^+; 9). Found: C, 71.32; H, 7.14%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

Reaction of Alkadienol 3a with CO_2 in the Presence of a Stoichiometric Amount of $PdCl_2$. A mixture of **3a** (1.0 mmol), $PdCl_2$ (1.0 mmol), and K_2CO_3 (2.0 mmol) in DMAc (2 cm^3) was heated at 80°C for 5 h under the pressure of CO_2 (40 atm). After the reaction, the mixture was taken up in diethyl ether and washed

with excess 1 M HCl. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was submitted to column chromatography on silica-gel eluting with hexane/ethyl acetate (3:1) to give **5l** (62%).

4,4-Dimethyl-5-(1-(2,2-dimethyl-2,5-dihydrofuran-4-yl)ethenyl)-1,3-dioxolan-2-one (5l). IR (neat) 1800 (C=O), 1640, 1600, 1270, 1080, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.28 (s, 3H, Me), 1.34 (s, 6H, Me), 1.64 (s, 3H, Me), 4.74 (d, J = 12.0 Hz, 1H, one H of CH_2), 4.87 (d, J = 12.0 Hz, 1H, the other H of CH_2), 5.11 (s, 1H, one H of H_2C=), 5.19 (s, 1H, the other H of H_2C=), 5.45 (s, 1H, HC–O), 5.68 (s, 1H, =CH); ^{13}C NMR ($CDCl_3$) δ = 22.52, 27.19, 27.61, 27.79, 73.74, 83.60, 84.40, 89.03, 115.30, 132.11, 133.94, 135.08, 153.63; GC-MS (70 eV) *m/z* 43 (100), 77 (23), 119 (23), 161 (48), 223 (38), 238 (M^+; 1). Found: C, 65.04; H, 7.56%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.65%.

General Procedure for the Preparation of Six-membered Ring Carbonate 7 from Alkadienol 6. A mixture of **6** (2 mmol), phenyl iodide (2 mmol), [$Pd(PPh_3)_4$] (0.04 mmol), K_2CO_3 (3 mmol), and DMAc (4 ml) was placed in an autoclave and heated at 100 °C under pressured CO_2 (40 atm). After 8 h, the mixture was taken up in diethyl ether and filtered. The organic layer was washed with 5 ml each of 1.0 M HCl for 5 times and 10 ml each of 2.0 M sodium sulfate for 3 times. The organic layer was concentrated in vacuo and the residue was submitted to column chromatography on silica gel eluting with hexane/ethyl acetate to give **7**.

4-(1-Phenylethenyl)-1,3-dioxan-2-one (7a). IR (neat) 1748 (C=O), 1673, 1248, 1226, 1195, 1131 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.90—1.97 (m, 1H, one H of CH_2–C–O), 2.15—2.20 (m, 1H, the other H of CH_2–C–O), 4.36—4.41 (m, 2 H, CH_2–O), 5.46 (dd, J = 8.2 and 3.7 Hz, 1H, HC–O), 5.48 (s, 2H, H_2C=), 7.32—7.38 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 26.37, 66.39, 79.29, 115.62, 126.84, 128.50, 128.85, 137.76, 145.33, 148.68; GC-MS (70 eV) *m/z* 44 (31), 51 (33), 77 (47), 103 (100), 104 (57), 115 (34), 129 (37), 131 (44), 160 (14), 204 (M^+; 14). Found: C, 69.74; H, 6.08%. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92%.

5-Methyl-4-(1-phenylethenyl)-1,3-dioxan-2-one (7b). A mixture of *cis* and *trans* isomers. IR (neat) 1752 (C=O), 1208, 1032 cm^{-1}. Found: C, 71.19; H, 6.69%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%.

***cis*-Isomer.** ^1H NMR ($CDCl_3$) δ = 0.92 (d, J = 6.8 Hz, 3H, Me), 2.06—2.13 (m, 1H, C*H*Me), 4.04 (dd, J = 10.8 and 9.6 Hz, 1H, one H of CH_2C–O), 4.29 (dd, J = 10.8 and 4.4 Hz, the other H of CH_2C–O), 4.95 (d, J = 8.6 Hz, 1H, =C–CH), 5.45 (s, 1H, one H of H_2C=), 5.51 (s, 1H, the other H of H_2C=), 7.30—7.38 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 12.50, 29.75, 71.53, 87.04,119.50, 127.37, 128.34, 128.68, 138.10, 144.67, 148.60; GC-MS (70 eV) *m/z* 42 (39), 44 (57), 51 (32), 77 (51), 103 (100), 104 (53), 128 (39), 129 (63), 145 (53), 218 (M^+; 11).

***trans*-Isomer.** ^1H NMR ($CDCl_3$) δ = 0.92 (d, J = 6.8 Hz, 3H, Me), 2.06—2.13 (m, 1H, C*H*Me), 4.17 (dd, J = 10.8 and 2.3 Hz, 1H, one H of CH_2C–O), 4.53 (dd, J = 10.8 and 3.4 Hz, the other H of CH_2C–O), 5.51 (s, 1H, =C–CH), 5.53 (s, 1H, one H of H_2C=), 5.57 (s, 1H, the other H of H_2C=), 7.30—7.38 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 9.73, 27.75, 73.24, 81.04, 115.07, 126.65, 128.45, 128.87, 137.97, 143.28, 148.42; GC-MS (70 eV) *m/z* 42 (72), 44 (60), 77 (60), 103 (100), 104 (75), 129 (58), 145 (74), 218 (M^+; 11).

4,4-Dimethyl-6-(1-phenylethenyl)-1,3-dioxan-2-one (7c). Mp 81—83°C. IR (KBr) 1724 (C=O), 1285, 1213, 1139 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.41 (s, 3H, one of Me_2), 1.51 (s, 3H, one of Me_2), 1.80 (dd, J = 12.4 and 14.2 Hz, 1H, one H of CH_2C–), 2.01 (dd, J = 14.2 and 3.0 Hz, 1H, the other H of CH_2C–), 5.41 (dd, J = 12.4 and 3.0 Hz, 1H, HC–O), 5.43 (s, 1H, one H of H_2C=), 5.54 (s, 1H, the other H of H_2C=), 7.34—7.36 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 26.24, 29.66, 38.63, 76.58, 81.02,115.49, 126.83, 128.31, 128.73, 137.89, 145.51, 149.14; GC-MS (70 eV) *m/z* 41 (23), 43 (55), 44 (23), 51 (21), 77 (36), 103 (71), 104 (100), 129 (20), 130 (35), 132 (21), 232 (M^+; 8). Found: C, 72.59; H, 7.40%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

Preparation of Five-Membered Ring Carbonate 9 from Alkadienol 8. A mixture of **8** (1 mmol), phenyl iodide (1 mmol), [$Pd(PPh_3)_4$] (0.02 mmol), K_2CO_3 (1.5 mmol), and DMAc (2 ml) was placed in an autoclave and heated at 120 °C under compressed CO_2 (40 atm). After 20 h, the mixture was taken up in diethyl ether and filtered. The organic layer was washed with 2.5 ml each of 1.0 M HCl for 5 times and 5 ml each of 2.0 M sodium sulfate for 3 times. The organic layer was concentrated in vacuo and the residue was submitted to column chromatography on silica gel eluting with hexane/ethyl acetate (5 : 1) to give **9** (48%).

(*E*)-4,4-Dimethyl-5-(3-phenyl-1-propenyl)-1,3-dioxolan-2-one (9). IR (neat) 1796 (C=O), 1634, 1267, 1188, 1014 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.33 (s, 3H, one of Me_2), 1.48 (s, 3H, one of Me_2), 3.45 (d, J = 6.6 Hz, 2H, CH_2), 4.67 (d, J = 7.9 Hz, 1H, HC–O), 5.50 (dd, J = 15.4 and 7.9 Hz, 1H, =CH–C–O), 6.08 (dt, J = 15.4 and 6.6 Hz, 1H, CH_2C*H*=), 7.15—7.30 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ = 22.19, 25.81, 38.56, 84.28, 85.92, 122.56, 126.55, 128.53, 128.65, 137.80, 138.45, 153.88; GC-MS (70 eV) *m/z* 43 (42), 70 (37), 115 (92), 129 (100), 130 (45), 145 (24), 157 (17), 172 (8), 232 (M^+; 7). Found: C, 72.58; H, 7.01%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

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